A metamict, thorium-rich magnesium phosphate from Overntjern, Modum, Norway

Gunnar Raade

Introduction

The interesting suite of magnesium phosphate minerals occurring at two of the Modum magnesite-serpentine deposits (Tingelstadtjern and Overntjern) was reviewed by Raade (1999). The minerals are althausite, holtedahlite, heneuite, raadeite and phosphoellenbergerite. A metamict, thorium-rich magnesium phosphate from Overntjern was briefly mentioned in the same paper. A more detailed description of this mineral is the purpose of the present report.

The metamict Mg phosphate is relatively rare and occurs as glassy, rounded inclusions in enstatite, up to about 5 mm in size. It has a brownish colour and is often turbid by submicroscopic inclusions. This mineral must not be confused with a dark brown, thorium-rich apatite which is quite typical of the Overntjern deposit. A partial electron-microprobe (EMP) analysis of this apatite was published by Raade (1986).

Three different samples of the metamict mineral were investigated at various times in the past. Energy-dispersive (EDS) EMP analyses of sample **OV-2** were performed in 1978 using an ARL-EMX instrument at *Sentralinstituttet for industriell forskning* in Oslo. It was reanalysed in 1982 with an ARL microprobe at the Mineralogical-Geological Museum, University of Oslo. A second sample, **OV-M**, was analysed at the museum in 1984. The third sample, **OV-1**, was analysed in wavelength-dispersive (WDS) mode in 1987 with a Camebax Microbeam instrument at the Mineralogical-Geological Museum. The EDS analyses were found to be of inferior quality by today's standards, and in the WDS analyses, arsenic was omitted. New EMP analyses were therefore performed on all three samples, as reported below.

The following data on X-ray diffraction and physical properties were obtained from sample OV-2 in 1977.

X-ray powder diffraction

The mineral was subjected to X-ray powder-diffraction investigation with a 9 cm Debye-Scherrer camera, using Mn-filtered Fe radiation. The unheated mineral gave a blank film (no. 23801), attesting to its metamict amorphous state. Material heated in air (film no. 23870) and in nitrogen (film no. 24484) at 1000°C gave similar X-ray powder patterns that could be interpreted as a mixture of thorianite, ThO_2, and farringtonite, $Mg_3(PO_4)_2$.

Physical properties

The density was measured by heavy-liquid flotation. Grains of the mineral, washed in ethyl alcohol and dried, were immersed in 1,1,2,2-tetrabromethane (d = 2.96 g/cm^3, determined with a 10 ml pycnometer at 20°C). The liquid was diluted drop by drop with N,N-dimethylformamide until most of the inclusion-containing grains had sunk to the bottom, and a fair amount of grains were suspended in the liquid (only a few grains were still floating on the surface). The density of the diluted tetrabromethane was determined with a 5 ml pycnometer at 20°C to 2.79 g/cm^3.

The mineral is generally isotropic, just a few grains showed weak birefringence. The refractive index, determined by the immersion method (grain mounts in refractive liquids), is variable; most grains have a refractive index in the range 1.586 to 1.596.

The infrared spectrum was recorded with the mineral powder dispersed in heavy paraffin oil (Nujol). As expected for a metamict mineral, the spectrum is rather featureless. There is a broad absorption roughly in the region 2800 to 3600 cm^{-1}, due to O–H stretching of H_2O, and a minimal absorption around 1600 to 1700 cm^{-1}, due to bending of the H_2O molecule. A more distinct but broad absorption with a maximum absorbance at 1050 cm^{-1} reflects the phosphate group.

Chemical investigations

Wavelength-dispersive analyses were performed with a Cameca SX100 electron probe equipped with five spectrometers, at 15 kV operating voltage and 10 nA probe current. The counting time was 10 s at both peak and background, and the beam diameter was 10 μm. The probe standards and peaks measured were: MgO (Mg$K\alpha$), wollastonite (Ca$K\alpha$ and Si$K\alpha$), Fe metal (Fe$K\alpha$), YPO_4 (Y$L\alpha$), synthetic glass with 14.97 wt% ThO_2 (Th$M\alpha$), $CePO_4$ (P$K\alpha$), GeAs (As$L\alpha$), fluorite (F$K\alpha$) and alforsite (Cl$K\alpha$). Uranium was sought but not detected; the Cl content is close to its detection limit. Iron is assumed to be divalent.

Water determination by the Penfield method on sample OV-2 gave 14.4 wt% H_2O. The same sample was investigated at *Institutt for Atomenergi* (Kjeller) in 1977. Measurement of natural γ-ray radioactivity (from ^{208}Tl) indicated a ThO_2 content of 12.4 wt%, assuming equilibrium between ^{232}Th and the radioactive daughter products. Neutron-activation analysis gave 14.5 wt% ThO_2 and less than 0.1 wt% UO_2.

Analytical results

Owing to its high water content, the mineral is relatively unstable under the electron beam. The results of the EMP analyses are presented in Table 1. The analytical total of sample OV-2, including the result of water determination, is 102.31 wt%. This elevated figure indicates that some water was lost during EMP analysis. Adding the same amount of water to the analytical data of sample OV-1 (which consists of three different grains, OV-1/1, OV-1/2 and OV-1/3), brings the analytical totals close to 100 wt%, indicating a somewhat higher actual H_2O content in this sample.

Samples OV-2 and OV-M have relatively homogeneous compositions with low standard deviations of individual oxides. OV-M is peculiar in being depleted in Ca and devoid of As. The three grains of sample OV-1 show comparatively large compositional variations within each grain and between the grains. Grains OV-1/1 and OV-1/2 have the lowest Th contents, and OV-1/3 is high in Ca. For OV-1/1, one analysis with as much as 8.95 wt% SiO_2 and a concomitantly low value for P_2O_5 has been singled out in Table 1 (OV-1/1-8). For OV-1/2, an analysis with a particularly high Y_2O_3 content of 4.67 wt% is also listed separately (OV-1/2-16). Grain OV-1/3 has a particularly large variation in FeO, from 2.05 to 5.59 wt%.

The cation contents were calculated on the basis of (Si+P+As) = 1 atom per formula unit and are given in the lower part of Table 1. The resulting cation sum of (Mg+Ca+Fe+Y+Th) is close to 2. The general chemical formula of the mineral can be expressed as $(Mg,Th,Fe,Ca,Y)_{2-x}(P,As,Si)O_4(OH,F,Cl)\cdot nH_2O$. Owing to their relatively large ionic radii, the cations Th, Y and Ca are normally not coupled with the smaller Mg cation. Since they in this case are minor constituents in terms of atoms per formula unit, the only possibility is to combine them with Mg (and Fe).

In the Modum magnesite-serpentine deposits, two other magnesium phosphate minerals have compositions with Mg:P = 2:1, namely althausite and holtedahlite with simplified formulae $Mg_2(PO_4)OH$. The precursor of the metamict magnesium phosphate is unknown but could be holtedahlite or possibly one of the three other polymorphs with composition $Mg_2(PO_4)OH$, synthesized by Raade (1990). It is not possible to know if the large amount of water in the metamict mineral, in excess of that needed to form OH, was introduced during the metamictization process, or if the precursor mineral was actually hydrated.

Acknowledgements
I am indebted to Roy Kristiansen for the infrared spectrum and the determination of water by the Penfield method. The expertise of Muriel Erambert was invaluable in the recently performed EMP analytical work. I gratefully acknowledge the financial support of Norsk Bergverksmuseum for the EMP investigation.

References

RAADE, G. (1986): Petrogenesis of serpentine-magnesite deposits at Modum, South Norway: A progress report. In: Metallogeny of basic and ultrabasic rocks (regional presentations). Theophrastus Publications S.A., Athens, 451-479.

RAADE, G. (1990): Hydrothermal syntheses of Mg2PO4OH polymorphs. Neues Jahrbuch für Mineralogie Monatshefte, 289-300.

RAADE, G. (1999): Et unikt mineralselskap av magnesiumfosfater fra magnesitt-serpentin-forekomster på Modum. Norsk Bergverksmuseum, Skrift 15, 11-14.

Table 1. Electron-microprobe analytical data (wt%) of metamict, thorium-rich magnesium phosphate from Overntjern, Modum.

	OV-2		OV-M		OV-1/1		OV-1/1-8	OV-1/2		OV-1/2-16	OV-1/3	
	N = 9	SD	N = 7	SD	N = 8	SD	N = 1	N = 7	SD	N = 1	N = 6	SD
MgO	32.41	0.97	34.05	0.41	33.56	1.91	36.22	34.54	1.44	32.02	30.18	1.89
CaO	0.90	0.46	0.04	0.02	1.44	0.59	0.60	0.56	0.17	0.34	2.74	0.80
FeO	1.80	0.13	2.33	0.08	2.62	0.22	3.00	2.66	0.18	2.37	3.27	1.72
Y_2O_3	1.06	0.16	1.09	0.12	1.60	0.39	0.92	1.78	0.20	4.67	0.81	0.09
ThO_2	14.78	0.36	15.60	0.27	10.47	1.70	8.03	10.94	1.77	11.86	15.22	0.59
SiO_2	0.67	0.20	0.69	0.22	1.07	0.64	8.95	1.74	0.68	1.81	1.18	0.95
P_2O_5	32.37	1.14	33.94	0.41	30.59	0.80	23.51	31.66	0.93	31.26	31.68	1.31
As_2O_5	3.55	0.68	b.d.l.		3.63	1.10	3.23	1.84	0.52	1.77	1.42	0.50
F	0.45	0.10	0.47	0.22	0.46	0.10	0.38	0.47	0.14	0.55	0.59	0.14
Cl	0.14	0.02	0.11	0.01	0.11	0.03	0.10	0.09	0.03	0.11	0.10	0.04
H_2O	14.4		n.d.		n.d.		n.d.	n.d.		n.d.	n.d.	
$-O\equiv F_2,Cl_2$	-0.22		-0.22		-0.21		-0.18	-0.22		-0.25	-0.27	
Sum	102.31		88.10		85.34		84.76	86.06		86.51	86.92	
Mg	1.60		1.73		1.72		1.75	1.74		1.63	1.56	
Ca	0.03		0.00		0.05		0.02	0.02		0.01	0.10	
Fe	0.05		0.07		0.08		0.08	0.08		0.07	0.10	
Y	0.02		0.02		0.03		0.02	0.03		0.09	0.02	
Th	0.11		0.12		0.08		0.06	0.08		0.09	0.12	
Sum	1.81		1.94		1.96		1.93	1.95		1.89	1.90	
Si	0.02		0.02		0.04		0.29	0.06		0.06	0.04	
P	0.91		0.98		0.89		0.65	0.90		0.90	0.93	
As	0.07		0.00		0.07		0.06	0.04		0.04	0.03	
Sum	1.00		1.00		1.00		1.00	1.00		1.00	1.00	

N = number of analyses. SD = standard deviation. n.d. = not determined. b.d.l. = below detection limit.